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# Combining state-of-the-art experiment and *ab initio* calculations for a better understanding of the interplay between valence, magnetism and structure in Eu compounds at high pressure

N. M. Souza-Neto<sup>a</sup> , D. Haskel<sup>b</sup>, R. D. dos Reis<sup>a,c</sup>  and F. C. G. Gandra<sup>c</sup>

<sup>a</sup>Brazilian Synchrotron Light Laboratory (LNLS), Campinas, SP, Brazil; <sup>b</sup>Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.; <sup>c</sup>Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), SP, Brazil

## ABSTRACT

We describe how first principle calculations can play a key role in the interpretation of X-ray absorption near-edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) spectra for a better understanding of emergent phenomena in condensed matter physics at high applied pressure. Eu compounds are used as case study to illustrate the advantages of this methodology, ranging from studies of electronic charge transfer probed by quadrupolar and dipolar contributions, to accurately determining electronic valence, and to inform about the influence of pressure on RKKY interactions and magnetism. This description should help advance studies where the pressure dependence of XANES and XMCD data must be tackled with the support of theoretical calculations for a proper understanding of the electronic properties of materials.

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Magnetism; X-ray spectroscopy; first principle simulations; XANES; XMCD

## 1. Introduction

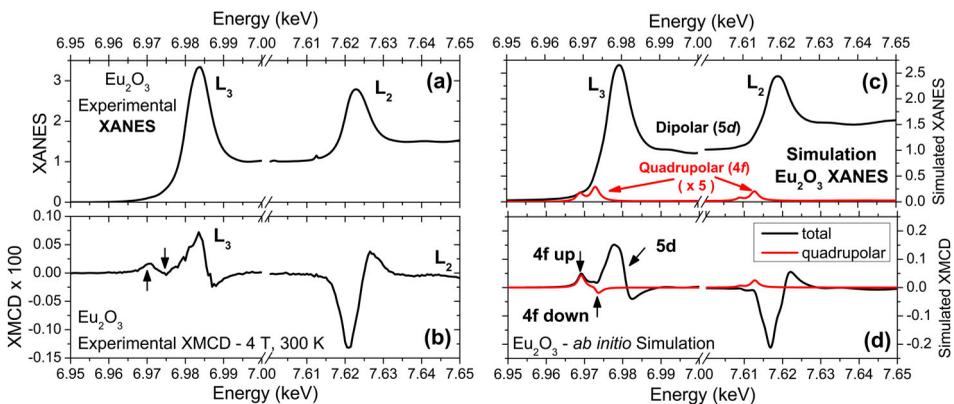
The electronic structure near the Fermi level in solids, particularly the density and orbital character of unoccupied states, dictates the spectral line shape of X-ray absorption near-edge structure (XANES). When circularly polarized X-rays are used, helicity-dependent XANES spectra give rise to X-ray magnetic circular dichroism (XMCD) that carries information about the spin-dependent electronic structure and magnetic properties.[1,2] Both XANES and XMCD are extensively used nowadays to give chemical, structural and magnetic information on materials under high applied pressure conditions.[3–10] While experimental methods have seen significant advances in the last decade including simultaneous measurements at low temperature and high magnetic fields,[3–5,11,12] data interpretation remains a major challenge. This is particularly exacerbated in the near-edge region of XANES and XMCD due to the low energy of excited photoelectrons and related strong sensitivity to the details of scattering potentials at neighbouring atom sites. Furthermore, the long mean free path of photoelectrons in this region enhances the importance of multiple scattering events. A proper understanding of experimentally

**CONTACT** N. M. Souza-Neto  [narcizo.souza@lnls.br](mailto:narcizo.souza@lnls.br)  Brazilian Synchrotron Light Laboratory (LNLS), Campinas, SP 13083-970, Brazil

observed features in the X-ray spectra can only be fully described with the support of first principle calculations of electronic structure and related calculations of XAS/XMCD spectra. Here, we discuss some key examples where *ab initio* simulations enabled an understanding of the evolution in the electronic structure of Europium compounds under applied pressure.

To illustrate some of the information contained in XANES and XMCD spectra, we shown in Figure 1 the  $L_{2,3}$ -edge experimental data for  $\text{Eu}_2\text{O}_3$  and compare it with theoretical simulations. Although  $\text{Eu}_2\text{O}_3$  is one of the most used chemical ingredients for growing complex rare earth compounds, it is still unexplored in terms of its unconventional magnetism and spin-dependent electronic structure. Its  $\text{Eu}^{3+}$  ions ( $J=L+S=0$ ,  $4f^6$  configuration) are often treated as non-magnetic even when presenting magnetic coupling.[13] From the XANES spectra, the energy position and intensity of the absorption peak (so-called white line) can be related to the chemical state (valence) and unoccupied density of states for orbitals participating in electric-multipole transitions in the X-ray absorption process. In particular, when we consider the dipolar and quadrupolar terms in the expansion of the light-matter interaction Hamiltonian that dictates the absorption cross section, it is possible to get orbital-selective information from the spectra. In this example, the dipolar term would inform about the  $5d$  orbitals and the quadrupolar term (second term in the multipole expansion) informs about the  $4f$  orbitals.[14] As seen in Figure 1(b), we have successfully probed the spin-dependent electronic structure of  $\text{Eu}_2\text{O}_3$  with XMCD measurements at the  $\text{Eu } L_{2,3}$  edges. By studying the magnetic field and temperature dependence of the XMCD signal, we identified the observed magnetism as being of the Van Vleck paramagnetic type.[15] Interestingly, the differences between  $L_3$  and  $L_2$  edges highlight the strong spin-orbit coupling that forces the large quadrupolar contribution ( $2p \rightarrow 4f$ ) to appear almost only at the  $L_3$  edge.[16] This is also supported by the *ab initio* simulations done with FDMNES code [17] that accurately predicts the positions and shape of the spin-up and spin-down quadrupolar ( $4f$ ) contribution.

In the following, we show how the ability to simulate the XANES and XMCD spectra with first principle calculations can help to assess a plethora of information in materials subjected to high pressures. Here, we use a few examples of our own work to demonstrate



**Figure 1.** Europium  $L_{2,3}$ -edges XMCD on  $\text{Eu}_2\text{O}_3$  high purity samples. The experimental and theoretical data are compared showing a remarkable agreement.

how to probe electronic charge transfer between  $4f$  and  $5d$  orbitals,[7] how to accurately determine valence of rare earths,[8,18,19] and how to probe the influence of pressure on magnetic interactions.[7,18]

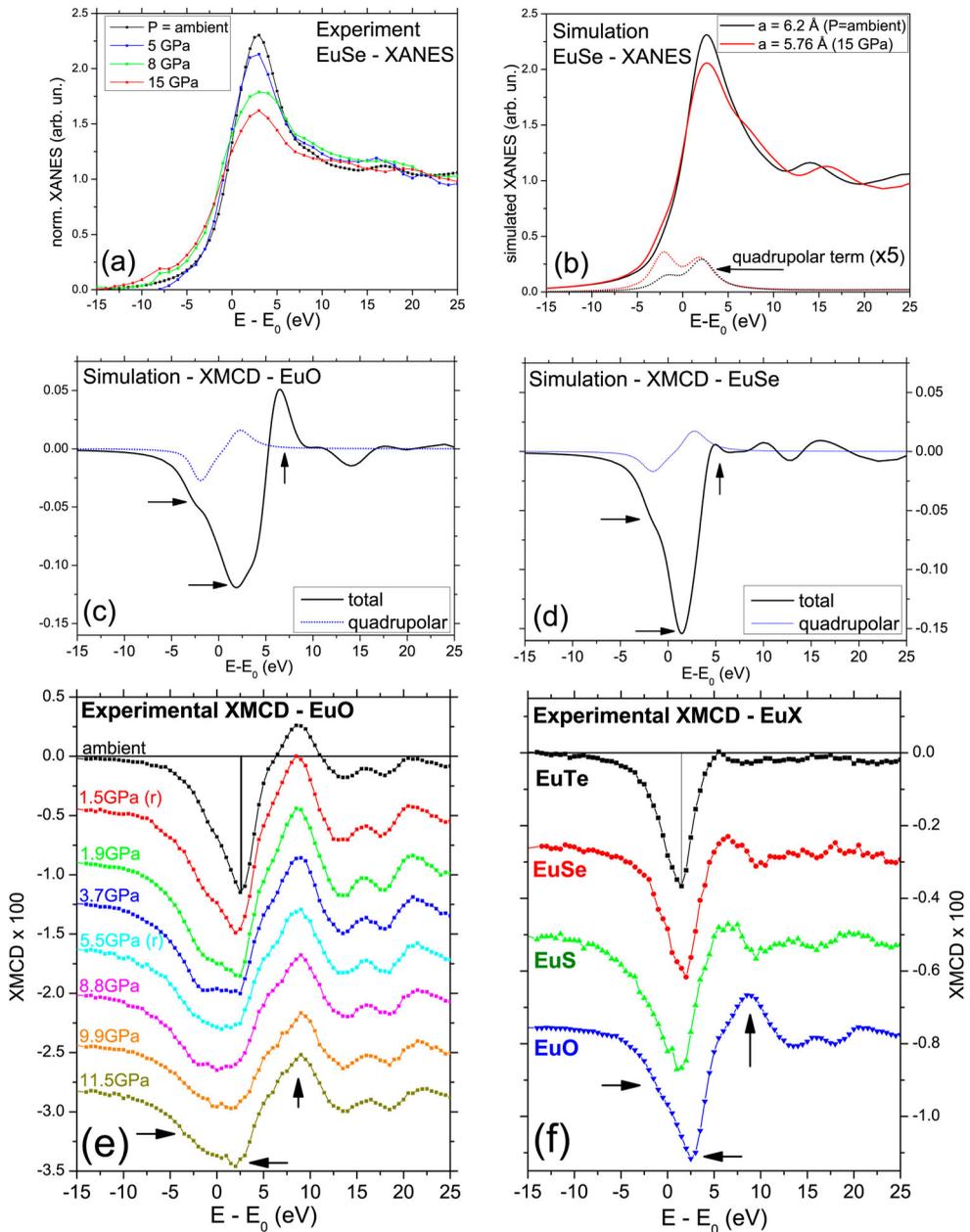
## 2. Methods

XANES and XMCD measurements at the Eu  $L_3$  and  $L_2$  edges were carried out in transmission geometry at beamline 4-ID-D of the Advanced Photon Source, Argonne National Laboratory.[11] The beam line is equipped with phase-retarding optics to convert the linear polarization of synchrotron radiation to circular.[20] Density functional theory *ab initio* calculations were performed using the WIEN2K implementation of the full-potential linearized augmented plane-wave (APW) method with a double-counting scheme and the rotationally invariant local density approximation (LDA) +  $U$  functional with  $U=7$  eV.[21] The size of APW + lo (APW with local orbital) basis was determined by the cut-off  $R(\text{mt})K(\text{max}) = 8$  (product of the Muffin Tin radius and maximum  $K$  value), with 99 irreducible  $k$ -points out of 1000- $k$ -point regular grid in the Brillouin zone. Only ferromagnetic structures were considered. The XANES and XMCD *ab initio* simulated spectra were obtained using the full multiple scattering approach implemented in the FDMNES code [17] including spin-orbit coupling.

## 3. Electronic mixing regulating magnetic properties in Europium monochalcogenides

Monochalcogenides  $\text{EuX}$  ( $X = \text{Te, Se, S, O}$ ) materials [22,23] have attracted renewed interest.[24–26] Although the ferromagnetic (FM) ordering temperature,  $T_C$ , is below 70 K in the bulk limiting its applications, a lattice contraction induced by pressure [27–29] and chemical doping [22,23,30] significantly increases  $T_C$  toward room temperature. For example,  $\text{EuS}$  reaches  $T_C \approx 290$  K at  $P=88$  GPa.[29] However, an understanding of the changes in electronic structure responsible for the strengthening of the indirect FM exchange interactions remained elusive with models alternatively centered on  $f$ - $d$ ,  $s$ - $f$  or  $p$ - $f$  mixing being proposed.[31–33] In this sense, a direct probe of the element- and orbital-specific electronic structure is key to conclusively explain the effect of lattice contraction upon the mechanism of indirect exchange regulating  $T_C$  in these materials.

We have used [7] XANES and XMCD experiments with the support of first principle calculations to exploit the element- and orbital-selectivity of the techniques in electric-dipole ( $2p \rightarrow 5d$ ) and electric-quadrupole ( $2p \rightarrow 4f$ ) channels to probe the spin-polarized electronic structure of Eu  $4f$  (valence) and  $5d$  (conduction) states as the lattice is contracted with chemical ( $\text{Te} \rightarrow \text{O}$ ) or physical pressure. Figure 2 shows representative XANES and XMCD data for Eu monochalcogenides as a function of physical- and chemical-pressure, all taken at the Eu  $L_3$  absorption edge ( $2p_{3/2}$  initial state) of these compounds. XANES and XMCD simulations carried out with the FDMNES code [17] are also shown. It was expected that a weak quadrupolar ( $2p \rightarrow 4f$ ) contribution dominated the photo-excitation process at the onset of X-ray absorption in these compounds, while dipolar contributions ( $2p \rightarrow 5d$ ) dominate at higher excitation energies. This assertion was confirmed by the FDMNES simulations, which facilitate assignment of XANES and XMCD spectral features to quadrupolar and dipolar channels. The lattice contraction induced by pressure



**Figure 2.** Experimental (a) and simulated (b) XANES spectra for EuSe as a function of applied pressure. Simulated XMCD spectra for EuO and EuSe are shown in (c) and (d). The pressure dependence of the XMCD spectra for EuO under physical pressure shown in (e) is compared with the dependence on chemical pressure induced by anion substitution from Te  $\rightarrow$  O in the XMCD spectra shown in (f). The two peaks in the quadrupolar contribution come from majority and minority  $4f$  states, separated by  $\approx 4.5$  eV. Quadrupolar contribution is probed through the magneto-optical selection rule for the  $2p \rightarrow 4f$  transition. The energy is referenced to the  $\text{Eu}^{2+} L_3$  absorption edge at 6.970 keV. Reproduced from [7].

results in a dramatic *decrease* in the amplitude of the main peak in XANES and XMCD spectra, which is dominated by dipolar contributions and probes the density of empty Eu  $5d$  states in the vicinity of the Fermi level. On the contrary, a concomitant *increase* in XANES and XMCD spectral weight is observed at lower energies where quadrupolar contributions dominate. This increase, which manifests an asymmetric broadening of the XMCD signal as the lattice is contracted with applied pressure or with anion substitution, is related to an increase in empty density of  $4f$  states. The spectral weight transfer from high to low energies observed in both XANES and XMCD data is evident that charge transfer from Eu  $4f$  to Eu  $5d$  states is taking place. Furthermore, the XMCD data unequivocally demonstrate that the newly formed empty  $4f$  states are spin-polarized.

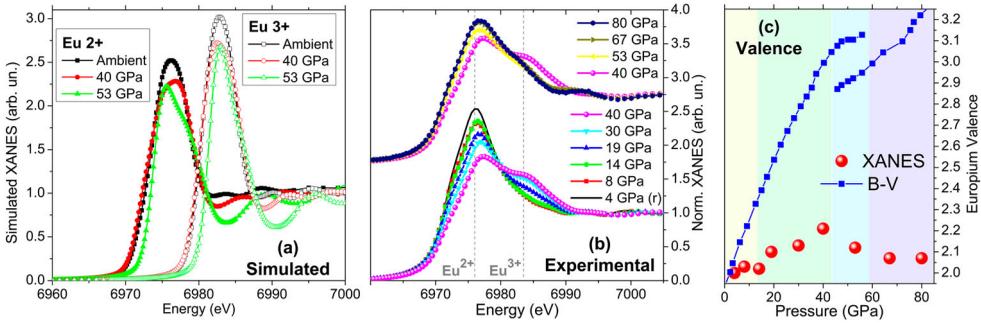
In summary, this combination of XANES and XMCD experiments under pressure combined with first principle calculations provided direct evidence that Eu  $4f$ – $5d$  electronic mixing is dramatically enhanced under physical pressure and dictates the FM ordering temperature,  $T_C$ . This mixing is much weaker when an equal lattice contraction is induced with anion substitution, a result of a concomitant increase in anion  $p$  and Eu ( $4f$ ,  $5d$ ) interactions that diminish the strength of indirect FM exchange.

#### 4. Probing valence changes induced by applied pressure

The phenomenon of mixed-valency in  $f$ -electron systems occurs when otherwise localized  $f$ -orbitals of Rare-Earth or Actinide elements hybridize in the solid with  $s, p, d$  electrons.[34] The onset of mixed-valency under applied pressure, chemical substitutions, or finite temperature has dramatic consequences on the macroscopic properties of  $f$ -electron systems including volume collapse,[35] quenched magnetism,[36] onset of superconductivity,[37,38] Kondo physics,[39] and quantum criticality.[37,38] Despite mixed valency being central to  $f$ -electron physics, the ability to directly probe this peculiar quantum electronic state at high pressures was limited. While XANES can provide access to this information, one has to be mindful that changes in local structure accompanying changes in valence ought to be deconvolved for proper valence assignment. A recent study on EuO uses a combination of XANES experiments and first principle calculations to address this issue.[8]

While standards with known valence state, such as  $\text{Eu}_2\text{O}_3$ , can be used to determine the degree of mixed valency, an accurate estimate must also consider the effect of changes in crystal structure upon the XANES spectra. With that in mind, lattice parameters determined by X-ray diffraction [8] were used in first principle calculations [7,17] to simulate XANES spectra as a function of pressure for both  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  electronic configurations as shown in Figure 3. These reference theoretical spectra were combined to match the experimental data and retrieve the ratio of  $2+/3+$  valence states. While the suppression of the main XANES peak can be attributed to the decrease in  $5d$  empty states,[7] the changes in spectral line shape in the high pressure phase are a result of the new crystal structure ( $B1 \rightarrow B2$  structural phase transition). The energy shift of the absorption edge is due to the contracted lattice. This method takes into account the different line shapes of XANES spectra corresponding to the two valences, which is ignored when XANES data are fitted with a linear combination of Gaussian peaks.[40]

Between 14 and 40 GPa, Eu is found to be in a mixed-valence state, reaching  $2.21+$  at 40 GPa. Remarkably, at higher pressures a *lower* valence state is abruptly recovered



**Figure 3.** (a) Ab initio simulated XANES spectra for EuO in the 2+ and 3+ valence configurations considering the lattice parameters determined by XRD at a few pressure points. An  $\approx 8$  eV threshold energy difference unequivocally distinguishes the two valence states. A linear combination of these calculated spectra was used to determine the experimental valence of the compound with a careful consideration of spectral shape induced by structural transitions. XANES measurements on EuO up to 80 GPa are shown in (b). XANES spectra in the 4–40 GPa pressure range show that fractional [ $P < 14$  GPa] and mixed-valence [ $14 < P < 40$  GPa] states are observed, with translated spectra showing the reentrant valence behavior at higher pressures [45–60 GPa]. (c) Comparison of the pressure dependence of europium valence determined by XANES and estimative from the bond-valence (B-V) method. Partially reproduced from [8].

concomitant with the B1  $\rightarrow$  B2 structural phase transition,[8] as shown in Figure 3; i.e. the  $\approx 7\%$  volume collapse is accompanied by a *decrease* in Eu valence. An increase in Eu–O bond length in the high pressure B2 phase as a result of the change in Eu coordination number from  $N=6$  (NaCl) to  $N=8$  (CsCl) allows for the reentrant valence transition to occur despite the sizable macroscopic volume contraction. Oftentimes, valence state is derived from structural data alone via BV sum rules,[41–43] which relate interatomic distances and coordination number to valence. As shown in Figure 3, the BV model commonly used to infer electronic valence from structural data fails to quantitatively describe the pressure-dependent mixed valency of EuO over the broad pressure range of the experiment, highlighting the need for directly probing electronic valence under pressure.

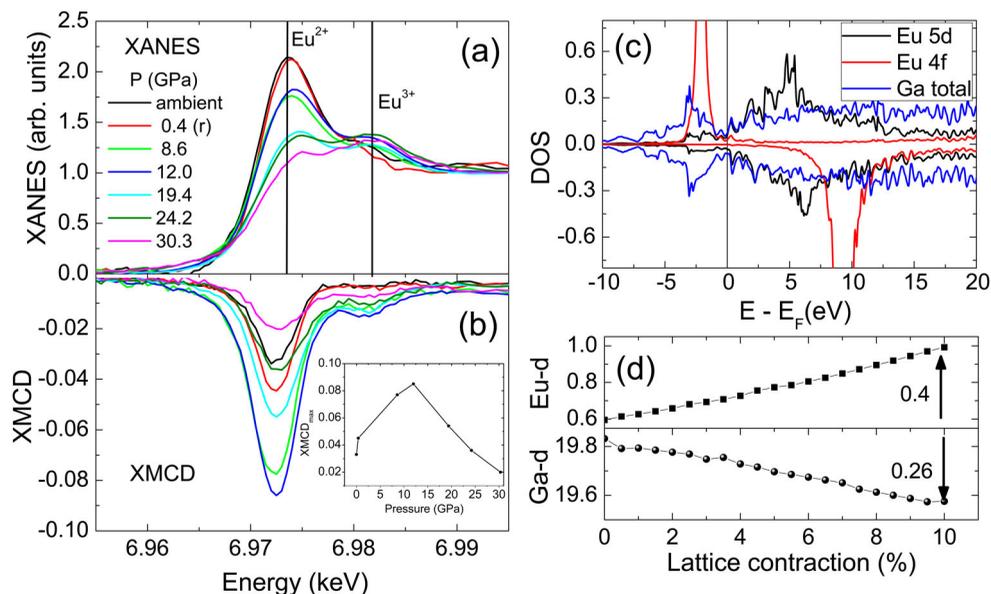
An additional illustration of the need to take into account changes in atomic structure when evaluating electronic valence is the case of Europium metal.[19] It was previously reported [44] that a strong valence change from 2+ towards 3+ takes place under pressure. However, accounting for changes in lattice structure [19] it was later shown that the valence of Eu does not show any significant change with pressure and that the spectral changes in the XANES were instead structural in origin. Although the valence remained 2+ up to pressures as high as 87 GPa, the magnetic ordering shows strong pressure dependence.[19] Proper interpretation of valence state is key to enable a full understanding of the electronic and magnetic properties, including emergence of superconductivity in Eu metal at pressures above 75 GPa.[45,46]

## 5. Pressure dependence of magnetic RKKY interactions in $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Ga}_4$

While XANES and XMCD measurements probe orbital occupancy and orbital polarization with orbital-specificity (dictated largely by dipole-selection rules connecting core and valence states), interpretation of such data is oftentimes difficult due to the presence of

orbital hybridization. Density functional calculations [21] of density of states and electronic occupation can be a great asset in supporting data interpretation. Case at hand is that of  $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Ga}_4$  compound [18] where a combination of data and theory allowed us to provide a more complete understanding of the electronic properties of the material. This system shows a continuous valence transition induced by pressure (see Figure 4). A combination of experimental data and first principle calculations of the XANES spectra allowed us to quantify the valence state as described above for  $\text{EuO}$ . In addition, one would like to understand how the mixed valency relates to the  $\text{Eu-5d}$  occupations, specifically what are the deviations from fully ionic  $\text{Eu}^{2+}$  ( $[\text{Xe}]4f^7$ ) and  $\text{Eu}^{3+}$  ( $[\text{Xe}]4f^6$ ) electronic configurations as a result of hybridization. The results, summarized in Figure 4, show strong hybridization between  $\text{Eu-5d}$  and gallium orbitals. This is evidenced by the increase in  $\text{Eu-5d}$  occupation concomitant with the decrease of  $\text{Ga-3d/4p}$  occupation and by the strong overlap between  $\text{Eu-5d}$  and  $\text{Ga}$  density of states. It is also noteworthy that the increase in  $\text{Eu-5d}$  electronic occupation is higher than the decrease in  $\text{Ga}$  orbital occupation, indicating that charges are also transferred from  $\text{Eu-4f}$  to  $\text{Eu-5d}$  orbitals in agreement with the observed valence change of the  $\text{Eu}$  ion.

Looking at the field dependence of the Europium XMCD peak amplitude as a function of pressure,[18] the magnetization loops unquestionably showed an antiferromagnetic to ferromagnetic transition induced by pressure. The coercive field continuously increases up to 30 GPa, indicating that ferromagnetic interactions are strengthened by lattice contraction. The observed pressure dependence of the XMCD amplitude, ordering temperature



**Figure 4.** Europium  $\text{L}_3$  XANES (a) and XMCD (b) spectra obtained at  $T = 6$  K and  $\mu_0 H = 4$  T for a powdered  $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Ga}_4$  sample as a function of applied pressure. The characteristic XANES peaks of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  are identified. (r) indicates measurement done after pressure release. Inset: XMCD peak amplitude as a function of applied pressure. (c) Calculated density of states for  $\text{Eu 5d}$ ,  $\text{Eu 4f}$  orbitals and  $\text{Ga}$  total DOS showing electronic hybridization between  $\text{Eu-5d}$  and  $\text{Ga}$  orbitals; (d) Electronic occupation numbers for  $\text{Eu-5d}$  and  $\text{Ga-3d}$ , for the total of atoms in the unit cell, as a function of lattice contraction. The simulations were done on the parent compound  $\text{EuGa}_4$ . Reproduced from [18].

and coercive field unequivocally shows that the magnetic interactions between Eu magnetic moments are drastically affected by lattice contraction, as do the overall electronic properties of the compound. To explain the evolution of magnetic properties with pressure, a simple mean-field treatment of carrier-mediated coupling described by Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions was evoked.[18] This compound crystallizes in the tetragonal  $\text{BaAl}_4$  structure with space group  $I4/mmm$  where Eu planes are stacked between Ga planes.[18] The interplanar interactions between Eu planes are therefore mediated by the intervening Ga atoms, with the strength of RKKY coupling oscillating and decaying [47–50] as a function of the distance between the Eu planes. Superexchange interactions via the non-magnetic Ga atoms may also contribute to the coupling. The relevance of polarized Ga orbitals in mediating indirect exchange between Eu–Yb planes is further evidenced in the observation of Ga XMCD signal [18] at about 10 eV above the Fermi level, an energy where strong overlap between the Eu-4*f* and Ga orbitals is observed in the density of states calculations presented in Figure 4(c).

## 6. Summary

In summary, we have shown how the use of first principle calculations of X-ray absorption spectra and electronic density of states allows for a better understanding of XANES and XMCD spectra as a function of high applied pressure. The information obtained with this methodology cannot be obtained by inspection of the experimental data alone and in many cases prevents correct data interpretation. It is hard to over-emphasize the need for continued improvements in first principles codes, including treatment of electron correlations, as well as the need for fast computing infrastructure at user facilities for on-the-fly data analysis using theoretical tools. The emergence of fourth generation sources based on multi-bend achromat lattices and related high-brilliance X-ray beams will lead to significant growth in the application of high pressure techniques, including spectroscopic studies such as these presented here. It is expected that the use of *ab initio* simulations will become an integral part of XANES/XMCD data interpretation greatly improving the accuracy with which microscopic information about the atomic, electronic and magnetic properties of materials subjected to high pressures can be obtained.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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## ORCID

N. M. Souza-Neto  <http://orcid.org/0000-0002-7474-8017>

R. D. dos Reis  <http://orcid.org/0000-0002-2212-4173>

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